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Structural instabilities in bis(4-chlorophenyl)sulfone derivatives studied by Raman spectroscopy and deuteron NMR

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The molecular solid bis(4-chlorophenyl)sulfone (BClPS) is one of the few van der Waals crystals having a displacive, soft-mode driven, incommensurate (IC) phase transition. In this work, we present an experimental study of the structural and dynamical behavior at low temperatures of three molecular solids closely related to BClPS: phenylsulfone, perdeuterated bis(4-bromophenyl)sulfone (d-BBrPS), and a mixed crystal d-BBrPS/BClPS with a molar ratio $[d\text{-BBrPS/BClPS}]=0.15$. Measurements of ^{2}H nuclear-magnetic-resonance relaxation times in d-BBrPS as a function of temperature showed the onset of a dynamical process between 157 and 148 K, similar to that observed in the phase transition of BClPS at 148 K. The temperature evolution of the relaxation rate is described in terms of the spectral density associated with a soft phonon with central-peak effects, using identical dynamical parameters measured for BClPS by neutron scattering. Neither loss of spatial periodicity nor symmetry change were detected in d-BBrPS below 148 K. For the mixed crystal, an IC phase was detected at low temperature, similar to that of BClPS but with spatial distortions of smaller amplitude.

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I. INTRODUCTION

In contrast to ionic solids, there are few examples of organic molecular crystals undergoing displacive phase transitions (PT) to incommensurate (IC) phases. The soft-mode driven IC PT of the organic crystal bis(4-chlorophenyl)sulfone (BClPS) has been the subject of many studies, due to its relatively high transition temperature ($T_I=148\,\mathrm{K}$) and the persistence of the IC state in a broad temperature range, at least down to 5 K.[1–7] The crystal structure of BClPS at room temperature is monoclinic $I2/a$, $Z=4$.[8] Below T_I, this structure is IC modulated along the monoclinic axis due to the condensation of a low damped soft mode with $\mathbf{q}\simeq 0.78\,\mathbf{b}^*$, far from symmetry points in the Brillouin zone.[3,9] The modulation involves displacements of the molecular center of mass, orientations, and interphenyl angles. Simple microscopic models of atom-atom interactions are able to predict the mechanical instability of a Λ_2 acoustic phonon in BClPS,[10] giving values for the wave vector and molecular displacements that are in remarkable agreement with experimental measurements of the soft-phonon wave vector and condensed phonon displacements in the IC phase,[3] respectively.

On the other hand, it is known that many organic crystals closely related to BClPS undergo complicated sequences of PTs, of a continuous and quasicontinuous nature.[11–13] As in BClPS, the "butterfly-like" biphenyl molecules in these solids are closely packed, forming chains along their C_2 symmetry axes. Therefore, a question to be addressed is to what extent this particular molecular packing is intrinsically related to the onset of PT and the loss of periodicity. Recently, Schneider *et al.* discussed the role of the intra and intermolecular interactions on the instability of the room-temperature structure of BClPS.[10] The results of lattice-dynamics calculations performed on BClPS and other closely related substituents suggested that this kind of molecular packing possesses an intrinsic instability involving the phonon at $\mathbf{q}\simeq 0.75\,\mathbf{b}^*$ on the lowest Λ_2 acoustic branch.[10] The wave vector and symmetry of the phonon at the deep local minimum are largely independent of the intramolecular interactions.[10] Therefore, the balance of intermolecular interactions is the determinant factor for the condensation of the soft phonon and the characteristics of the low-temperature phase in the solid specifically considered. This situation is analogous to the well-known phase transition in the A_2BX_4 group of ionic solids.[14] From an experimental point of view, temperature, pressure and atomic substitutions in selected positions are potential variables to modify the intermolecular couplings in order to explore the appearance of lattice instabilities and the structural ways they are resolved in each crystal of the group.

The aim of this work is to provide experimental information about the low-temperature structural and dynamical behavior of several solids related to BClPS, to be compared with the conclusions of the lattice-dynamics analysis. The molecular solids bis(4-bromophenyl)sulfone (BBrPS), phenylsulfone (PS), and binary mixed crystals BBrPS:BClPS were analyzed using Raman spectroscopy and deuteron nuclear-magnetic-resonance (NMR) spin-lattice relaxation-time (T_1) measurements. Molecules of BBrPS and PS are closely related to BClPS having, respectively, Br and H substitutions instead of Cl in both *para* positions of phenyl groups. BBrPS is a very interesting subject of study because it is isostructural to BClPS at room temperature[8] and the lattice-dynamics analysis suggested the possibility of phonon instabilities.[10] These calculations for BBrPS showed an anomaly deep on the lowest Λ_2 acoustic branch at $\mathbf{q}=0.76\,\mathbf{b}^*$, as in BClPS. Also, the molecular displacements involved in this phonon are the same as those corresponding to the anomaly of BClPS at $\mathbf{q}=0.75\,\mathbf{b}^*$ on the same branch.[10] To the best of our knowledge, there are no previous studies on the structural or dynamical behavior of BBrPS at low temperature. On the other hand, PS crystallizes in a less symmetrical array with respect to BClPS [$P2_1/c$, $Z=4$

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(Ref. 15)] and despite the similarity in molecular structure, no anomalies were observed in the calculated dispersion branches of this solid.[10] So, lattice-dynamics calculations do not show any mechanical instability that could lead to PT at lower temperatures.

On the other hand, when solid solubility is possible, dissolution of guest molecules in a host lattice is an interesting way to perturb locally the balance of intermolecular interactions. In the present work, relatively low concentrations of BBrPS molecules were diluted in the BClPS host lattice indicating the feasibility of this procedure. The structural and vibrational properties of the obtained mixed crystals were studied by Raman spectroscopy, in order to evaluate the effect of the perturbation on the IC modulation.

II. EXPERIMENTAL PROCEDURES

Samples of PS, BClPS, and perdeuterated BBrPS were provided, respectively, by Aldrich (99%), Fluka (purum grade), and Medical Isotopes, Inc. (purity 99%, deuteration 99%) and subjected to additional recrystallization processes. Mixed crystals of d-BBrPS/BClPS were prepared following the method of dissolution recrystallization.[16] Fine powders of pure compounds were mixed at the desired molar ratios and dissolved in benzene. The solvent was evaporated under a gentle nitrogen flux and continuous stirring of the solution was done to avoid separation of components. The precipitate was powdered and stored under dry atmosphere at room temperature until the experiments were performed. Three samples were prepared with molar ratios $x=[d\text{-BBrPS/BClPS}]$ of 0.07, 0.15, and 0.30.

The homogeneity of pure components and mixed crystals was characterized by powder x-ray diffractometry, performed with a Rigaku Rotaflex RU200B diffractometer with nickel-filtered Cu $K\alpha$ radiation (1.540 Å). Some degree of structural relaxation was detected for mixed crystals until 20 days after preparation, involving small shifts of some reflections at low 2θ values. Samples were monitored by x-ray diffraction over four months, but no additional changes were detected. All the studies were done on samples that were more than three months old.

Raman measurements were carried out using the 514-nm line of an Ar-ion laser as the exciting source. A Spex double monochromator equipped with single-photon counting and a homemade data-acquisition system were used for the detection of the scattered radiation. The spectral resolution of the measurements was of 0.25 cm^{-1}. Low-temperature studies were performed by using a Janis helium flux cryostat.

Deuteron NMR measurements were performed at a field of 9.4 T with a Varian Unity INOVA spectrometer and a Doty wideline NMR probe. Temperature was varied by gas nitrogen flux and controlled within 0.5° during each experiment. The Zeeman spin-lattice relaxation time (T_1) was measured on one of the edge singularities of the ^{2}H powder pattern, associated to crystallites with an angle of 90° between the principal value of the electric-field gradient tensor and the external static magnetic field. The saturation-recovery pulse sequence ($\pi/2|_{0°}$-τ-$\pi/2|_{0°}$-τ_E-$\pi/2|_{90°}$) was used, generating a quadrupolar echo to monitor the recovery of the magnetization. Radio frequency pulses of 4-μs duration were used. Due to the long values recorded for T_1, measurements on the ^{2}H-enriched BBrPS samples were done without signal averaging. The single-exponential recovery of magnetization was monitored at more than 20 values of τ for each temperature, and T_1 values were extracted through the fitting of a three-parameter standard expression.

III. RESULTS

A. Bis(4-chlorophenyl)sulfone (BClPS)

BClPS was considered in this study as our prototype system in order to check how structural changes associated with its well-known IC PT at $T_I = 148\,\text{K}$ can affect the Raman spectrum of a powder sample. Figure 1(c) shows some representative low-frequency Raman spectra of a powder BClPS sample at different temperatures. The temperature evolution of the detected Raman-active vibrations is plotted in Fig. 2(a). The frequencies were determined by multiple-Lorentzian deconvolution of the powder spectra. As it was discussed in previous studies,[2,10] the lowest Raman frequencies are associated with modes involving not only basic molecular translations and rotations, but also internal degrees of freedom of low frequency that are able to couple with them. This is certainly the case of three internal modes of BClPS related to interphenyl motions: the interphenyl symmetric bending and the antisymmetric and symmetric phenyl torsions along the *S-C* (*para*) axis. In the free molecule, these vibrations have frequencies less than 60 cm^{-1}. Then, considering nine degrees of freedom for each of the two BClPS molecules in the primitive cell (C_2-point symmetry), nine low-frequency Raman-active vibrations result: 4Ag+5Bg. As seen in Figs. 1(c) and 2(a) these nine vibrations are easily detected in the spectra of the high-temperature phase. For temperatures lower than 130 K several continuous changes can be noted in the spectra, involving the appearance of new bands, the splitting of high-temperature lines, and the rearrangement of intensities in the 100–120 cm^{-1} region. The activation of new lines in the Raman spectrum is associated with the loss of spatial periodicity in the IC phase. The static structural distortions associated with the IC spatial modulation break the selection rules associated with the room-temperature space group. The more intense and well-resolved new bands appear around 40 cm^{-1}, detectable from 125 K down to the lowest temperatures. Many other vibrations exhibit changes in their temperature dependence with respect to the high-temperature phase. All these observations are compatible with previous Raman measurements performed on a single BClPS crystal[2] in the same temperature range. Therefore, through the analysis of the powder Raman spectrum, it is possible to detect with confidence the lost of spatial periodicity in the BClPS lattice after the phase transition. Nevertheless, the transition temperature cannot be obtained with precision from these measurements, due to the fact that splittings of the bands or changes in their temperature behavior are only appreciable for temperatures where the spatial distortions have enough amplitude. Raman spectroscopy, even on a single BClPS crystal,[2] is less sensitive in determining transition temperature than other experimental

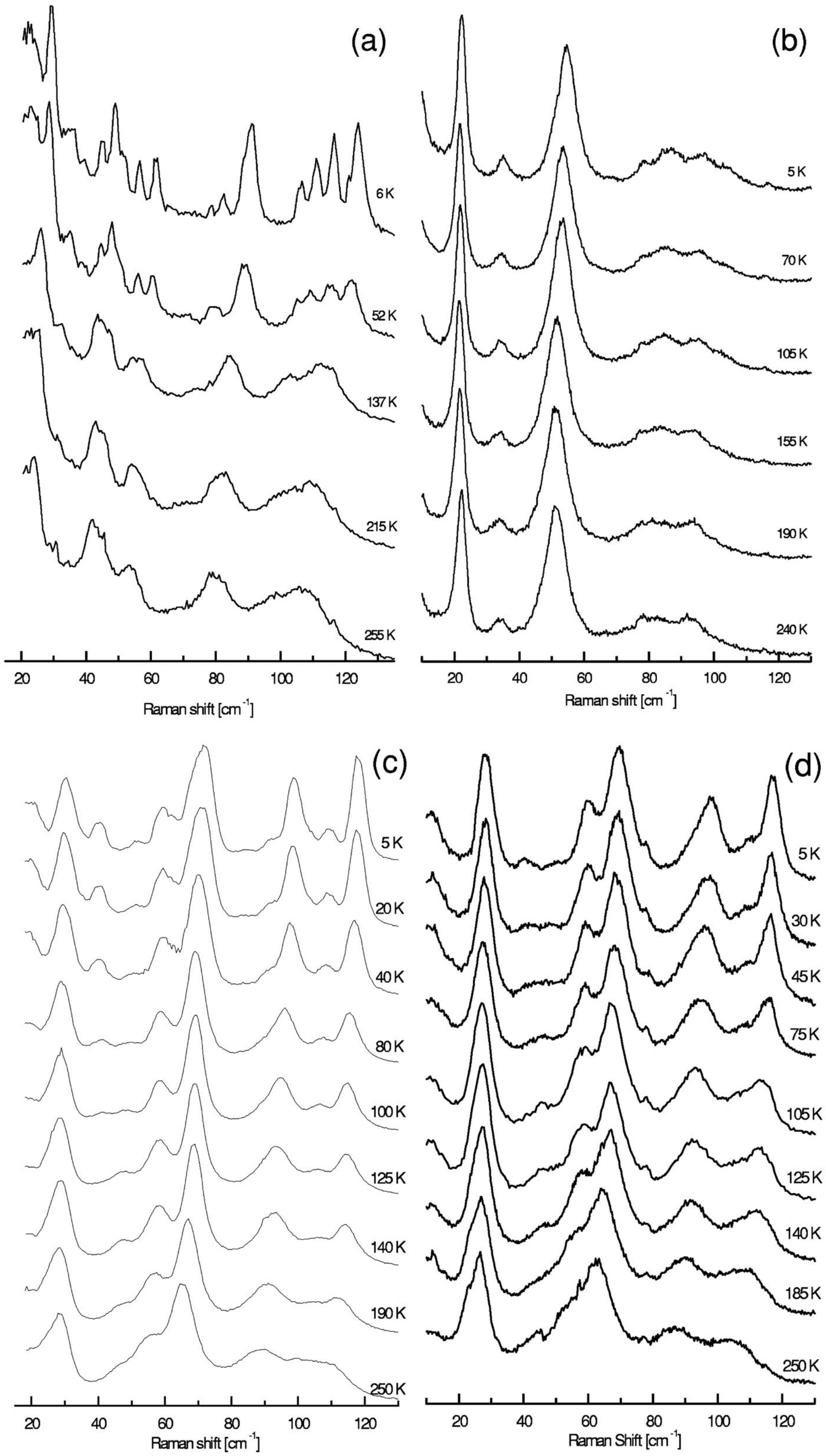

FIG. 1. Representative Raman spectra at different temperatures of polycrystalline samples: (a) PS, (b) d-BBrPS, (c) BClPS, and (d) mixed crystal $[d\text{-BBrPS/BClPS}]=0.15$.

techniques, such as for example calorimetry[17] or nuclear quadrupole resonance (NQR).[7]

B. Phenylsulfone (PS)

For the PS crystal, mixing of low-lying internal vibrations with lattice modes is also expected as in BClPS. So, considering the crystallographic data of PS at room temperature ($Z=4$; C_1 molecular point symmetry[15]) and the molecular model with nine degrees of freedom, 18 vibrational modes are expected to be observed in the Raman spectrum ($9A+9B$). Figure 1(a) shows the Raman spectra of PS as a function of temperature. Seventeen vibrations can be de-

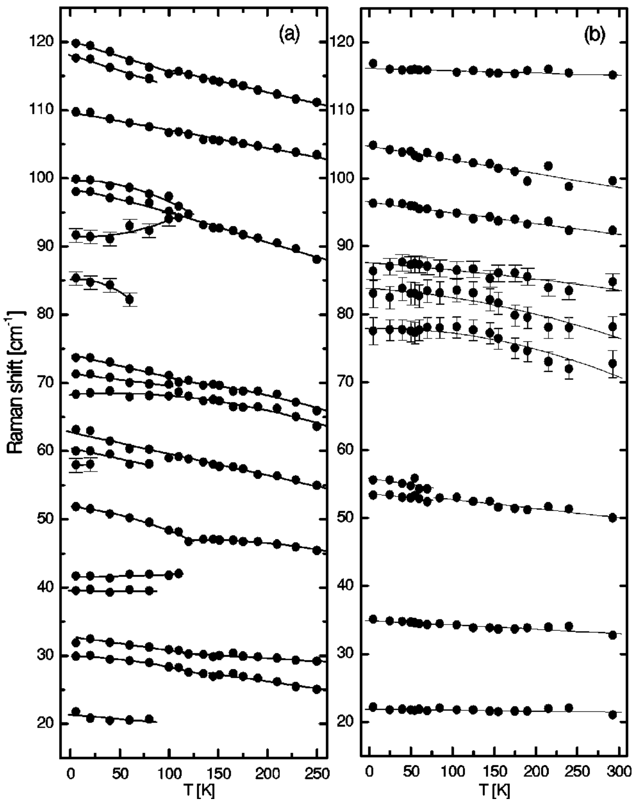

FIG. 2. Frequencies of Raman vibrations of (a) BCIPS and (b) d-BBrPS, as a function of temperature.

tected with confidence at the lowest temperatures, where lines are considerably narrowed. The temperature behavior of the phonon frequencies is that normally expected in slightly anharmonic crystals: an almost linear decrease in frequencies as temperature rises. From these observations, it can be concluded that the periodic room-temperature structure of PS remains stable down to 5 K. This result is in agreement with the lattice-dynamics analysis, where no anomalies in the calculated phonon branches were observed considering the room-temperature crystal structure and even a fully relaxed zero-Kelvin cell.[10]

C. Bis(4-bromophenyl)sulfone (BBrPS)

Due to the fact that BBrPS is isostructural with BClPS at room temperature, nine Raman-active modes are expected to be observed in the low-frequency spectrum. Accordingly, the spectra of BBrPS are rather similar to those of BClPS at high temperature, as seen in Figs. 1(b) and 1(c). After the narrowing of the 50-cm^{-1} band below 100 K, nine vibrations could be deconvoluted down to 5 K. The temperature evolution of the vibrational frequencies of BBrPS is plotted in Fig. 2(b), evidencing a standard anharmonic behavior. Three bands between 70 and 90 cm^{-1} have an apparent change of temperature dependence at 150 K, but it is not a conclusive observation because these lines are weak and overlapped. Therefore, from these Raman spectroscopy data it can be concluded that BBrPS does not undergo any structural transition at low temperatures with noticeable spatial distortions. The symmetry of the unit cell of BBrPS is not affected, because no new Raman bands were observed. In particular, no IC modulations of the type observed in BClPS appear in BBrPS at low temperatures.

Considering the close structural relationship of BBrPS with BClPS, which exhibits a lattice instability, and the fact that dynamics calculations also suggested a soft-mode behavior, there is a motivation to probe the low-frequency phonon dynamics of BBrPS at low temperatures. Soft-phonon phenomena give rise to a diverging temperature behavior of the dynamic structure factor $S(\mathbf{q},\omega)$ at zero frequency near the transition temperature.[18,19] The NMR spin-lattice relaxation times are sensitive to these kind of processes in the megahertz spectral range, due to the proportionality between relaxation rates (T_1^{-1}) and spectral densities. Therefore, T_1 measurements in BBrPS could reveal if some of these critical dynamic processes were occurring. Deuteron NMR was considered in order to deal with shorter relaxation times with respect to ^{1}H, due to the quadrupolar coupling of deuterons with the fluctuating part of the local electric-field gradient. For deuterons, the Zeeman T_1 is given by

$$T_1^{-1}=\frac{3\pi^2}{2}\left(\frac{e^2qQ}{h}\right)^2[J_1(\omega_L)+4J_2(2\omega_L)],$$

where ω_L is the Larmor frequency (61.3 MHz at 9.4 T) and e^2qQ/h is the quadrupole coupling constant of the deuteron. The functions $J_i(\omega)$ are the spectral densities of the autocorrelation functions of the time-dependent parts of the quadrupolar Hamiltonian.[18,20] In the case of one-phonon processes, the spectral densities can be expressed as an integral over the first Brillouin zone of the phonon-scattering function as[18]

$$J_i(\omega)=\int A^i(\mathbf{q})S(\mathbf{q},\omega)d^3q, \tag{1}$$

where the $A^i(\mathbf{q})$ are geometrical slowly varying functions of $\mathbf{q}$ associated with the short-range quadrupole interaction. The spectral density contains an orientational dependence on the angle between the deuteron bond direction and the static magnetic field. In cases where the main contribution of these functions comes from one $\mathbf{q}$, as for example in a soft-mode condensation, the $A^i(\mathbf{q})$'s can be extracted out of the integrals, giving a proportional relationship between relaxation rates T_1^{-1} and the integral of the critically diverging scattering function $S(\mathbf{q},\omega)$. In these cases, the relaxation rate can be written as

$$T_1^{-1}=a_1\int S(\mathbf{q},\omega_L)d^3q+a_2\int S(\mathbf{q},2\omega_L)d^3q, \tag{2}$$

where a_1 and a_2 are factors depending on bond orientation and the coupling constant.

On the other hand, when phonon branches are almost temperature independent, it is possible to express the relaxation rate for Raman processes at high temperatures as $T_1^{-1}=BT^{\lambda}$, with $\lambda\approx-2$ and B is an empirical factor.[21] This dependence is referred as the "normal" background relaxation. The whole relaxation rate in the presence of critical phenomena should be written as

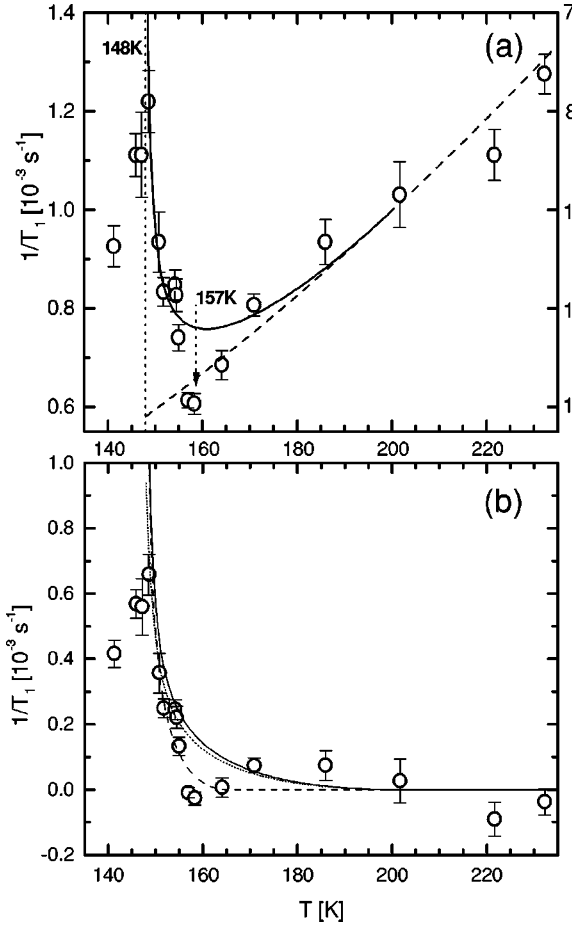

FIG. 3. Deuteron Zeeman spin-lattice relaxation time for *d*-BBrPS as a function of temperature. (a) Circles: experimental data. Full line: soft-phonon and central-peak model for $J_1(\omega L)$ with dynamical parameters of the IC phase transition of BCIPS. Dashed line: fitting of the background relaxation. Vertical dotted line: asymptote at 148 K. (b) Relaxation rates after subtracting the background contribution. Circles: experimental data. Full line: model for $J_1(\omega L)$. Dotted line: model for $J_2(2\omega L)$. Dashed line: model for $J_1(\omega L)$ and the assumption of $\delta=0$ for $T>165$ K.

$$T_1^{-1}=A_1\int S(\mathbf{q},\omega_L)d^3q+A_2\int S(\mathbf{q},2\omega_L)d^3q+BT^{\lambda}. \tag{3}$$

Measurements of the Zeeman T_1 for ^{2}H were carried out in a perdeuterated BBrPS sample down to 140 K. In spite of the quadrupole coupling, T_1 values in the scale of minutes were measured for deuterons of BBrPS. Figure 3(a) shows the measured relaxation rate T_1^{-1} as a function of temperature, where a notorious change of behavior can be observed around 150 K. From room temperature down to 157 K, the temperature behavior of T_1 is well described by the background relaxation term. On the other hand, an abrupt growth in the relaxation rate values occurs in the range 148–157 K, due to the appearance of an additional relaxation mechanism that dominates over the normal phonon background. On lowering temperature below 148 K, the relaxation rate decreases again.

A remarkable similar behavior has been observed around the normal-IC phase transition of BClPS for the T_1 of protons,[22] deuterons,[6] and also chlorine in pure ^{35}Cl-NQR experiments.[23,6,7] In those cases, the enhancement of the relaxation rate is caused by the low-frequency collective fluctuations prior to the IC PT, associated with phonon softening and central-peak processes. It must be noted that the measured values for the Zeeman T_1 of deuterons in BBrPS at 157 (beginning of the relaxation enhancement) and 148 K (measured maximum for the relaxation rate) are almost identical to those reported for BClPS at the same temperatures.[6]

In order to characterize the enhancement of ^{2}H relaxation in terms of a critical exponent ξ, several trial fittings of the power law $T_1^{-1}=C/(T-T_I)^{\xi}$ were carried out. The best results where obtained fixing T_I and considering a temperature range up to 8 K above T_I. In this way, satisfactory fittings of the power law where obtained only for T_I values ranging between 147.5 and 148.0 K. Fitted critical exponents resulting from these two limiting transition temperatures were respectively $\xi=0.63\pm0.05$ and 0.47 ± 0.05, which should be considered as extreme values consistent with our data set. It can be noted that an uncertainty of 0.5 K for T_I is still too broad to extract a critical exponent useful to discriminate between different models of phase transitions, such as for example the three-dimensional *XY* ($\xi=0.624$) or the mean-field ($\xi=0.5$) models.

An alternative approach to interpret the observed relaxation enhancement can be carried out considering the critical phonon response instead of a description in terms of critical exponents. In a recent work, inelastic-neutron-scattering (INS) data of BClPS were correlated with NMR relaxation rates.[6] The form of the scattering function $S(\mathbf{q},\omega)$ was explicitly considered and the integrals in Eq. (3) were numerically resolved. The scattering function was written in terms of two contributions:[6,19]

$$S(\mathbf{q},\omega)=S_{ph}(\mathbf{q},\omega)+S_{cp}(\mathbf{q},2\omega). \tag{4}$$

The first term corresponds to the response of a damped harmonic oscillator, with characteristic frequencies for the soft mode $\pm\omega_\infty(\mathbf{q},T)$ and the damping constant Γ,

$$S_{ph}(\mathbf{q},\omega)=\frac{k_BT}{\pi}\frac{\Gamma}{[\omega_\infty^2(\mathbf{q},T)-\omega^2]^2+\omega^2\Gamma^2}. \tag{5}$$

The second contribution corresponds to so-called central-peak phenomenon, arising from nonlinear dynamics effects near the transition temperature T_i. The soft mode decays into several modes, one of them being nonoscillatory, and decays exponentially with a time constant $1/\gamma$. The response associated to this process is[19]

$$S_{cp}(\mathbf{q},\omega)=\frac{k_BT}{\pi}\frac{\delta^2}{\gamma\omega_0^4(\mathbf{q},T)}\frac{1}{1+\omega^2\left(\dfrac{\omega_\infty(\mathbf{q},T)}{\omega_0(\mathbf{q},T)}\right)^4\left(\dfrac{1}{\gamma}\right)^2}. \tag{6}$$

The square of the soft-mode frequency can be written as a function of the renormalized frequency $\omega_0^2(\mathbf{q},T)$ as

$\omega_\infty^2(\mathbf{q},T)=\omega_0^2(\mathbf{q},T)+\delta^2$, where δ is the coupling strength between the soft mode and the purely relaxing mode responsible for the central peak. For wave vectors near a satellite at $\mathbf{q}_S$, the renormalized frequency can be expanded as $\omega_0^2(\mathbf{q},T)=a(T-T_I)+Dq^2$. Considering that all parameters in Eqs. (5) and (6) were determined in BClPS by INS, only the multiplicative factors in Eq. (3) and the exponent λ are free parameters to be fitted to data. As was reported in Ref. 6, an excellent agreement was observed between the temperature behavior of relaxation rates and the central-peak model for $S(\mathbf{q},\omega)$ in the IC-PT of BClPS.

Despite that there are no experimental studies of $S(\mathbf{q},\omega)$ for BBrPS, it is possible to check the compatibility of the measured relaxation rates with the predictions of Eqs. (3) and (4) considering the dynamic parameters determined for BClPS: $a=345\,\mathrm{GHz}^2/\mathrm{K}$, $D=8.5\times10^6\,\mathrm{GHz}\,\text{Å}^2$, $\gamma=2.5$ and $\Gamma=120\,\mathrm{GHz}$. The coupling strength δ was assumed as a linear function of temperature vanishing for $T>200\,\mathrm{K}$ as $\delta(T)=80\,\mathrm{GHz}\;(T-200\,\mathrm{K})/(T_i-200\,\mathrm{K})$, according to Ref. 6. The full-line trace in Fig. 3(a) is a plot of relaxation rates given by Eq. (3) assuming $A_1 \gg A_2$, i.e., only contributions of the spectral density $J_1(\omega)$ at the Larmor frequency and $T_I=148.0\,\mathrm{K}$. Only the amplitude factor A_1 was fitted for the critical contribution to relaxation ($A_1=1.8\pm0.1\,\text{Å}^3\,\mathrm{s}^{-2}\,\mathrm{J}^{-2}$). The fitted background relaxation parameters were $B=(4.2\pm0.1)\times10^{-8}\,\mathrm{K}^{-\lambda}\,\mathrm{s}^{-1}$ and $\lambda=1.9\pm0.1$. The agreement with the experimental data of BBrPS is remarkable, considering that the shape of the curve was determined solely by the dynamic parameters measured for BClPS. Figure 3(b) shows the critical contribution to relaxation rates after subtracting the background term. The dotted line corresponds to the case $A_1 \ll A_2$, i.e., only contributions from the spectral density $J_2(2\omega_L)$ at twice the Larmor frequency. As can be seen, both curves have nearly the same temperature dependence, and it is not possible to attribute the relaxation to only $J_1(\omega_L)$ or $J_2(2\omega_L)$. It is worth mentioning that by disregarding the central-peak contribution to $S(q,\omega)$ in Eq. (3) and keeping only the soft-phonon response it was not possible to reproduce the observed temperature dependence of T_1^{-1}.

Despite the scattering of T_1^{-1} data, it can be noted that the enhancement of relaxation rates in BBrBS seems to occur for temperatures lower than those in BClPS. Considering that the central-peak process dominates the observed temperature behavior, it is interesting to test the effect of reducing the onset temperature of the coupling δ, which is 200 K in BClPS, on the shape of the relaxation rate curve. In Fig. 3(b) the dashed line is the result of fitting the critical dependence fixing an onset temperature of 165 K, using the same strength of 80 GHz and assuming for simplicity only contributions from $J_1(\omega_L)$, i.e., $A_2=0$. The resulting multiplicative parameter is $A_1=1.7\pm0.1\,\text{Å}^3\,\mathrm{s}^{-2}\,\mathrm{J}^{-2}$. A slightly better agreement with the experimental data can be observed in this case, although this is not an accurate determination of the vanishing temperature of the coupling strength δ.

Finally, it should be mentioned that no changes were observed in the features of the ^{2}H-NMR powder pattern of BBrPS at any temperature, from room temperature to 140 K.

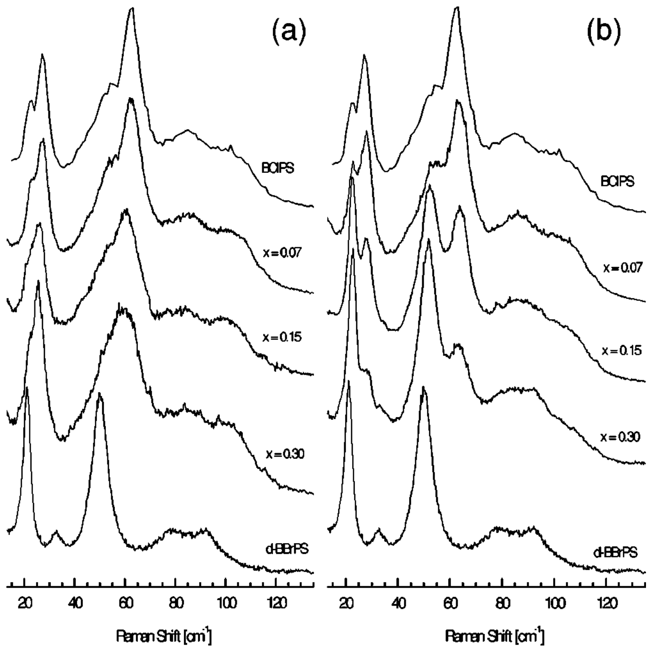

FIG. 4. Raman spectra of polycrystalline samples at room temperature. (a) Mixed crystals with different molar ratios $x=[d\text{-BBrPS/BCIPS}]$, obtained from dissolution recrystallization. (b) Mechanical mixtures with the same ratios *x*. Spectra from pure BBrPS and BCIPS are included for comparison in both cases.

D. Mixed crystals BBrPS/BClPS

Three mixed crystals were considered, with molar ratios *x* between BBrPS/BClPS taking the values 0.07, 0.15, and 0.30. In order to determine if phase segregation occurred in these samples, powder x-ray-diffraction analyses were performed. The observed diffraction patterns could not be decomposed as a superposition of the pure phase patterns. In fact, the number of Bragg reflections was the same as in the BClPS pattern. Only variations in intensity and positions of some reflections were detected. Therefore, it can be concluded that no appreciable degree of segregation occurred. As an additional test, Raman spectroscopy measurements were carried out in the three mixed crystals and also in finely ground mechanical mixtures of BBrPS/BClPS with the same molar concentrations. Figures 4(a) and 4(b), respectively, show the obtained spectra for both set of samples. For mechanical mixtures, vibrations of individual phases can be readily identified in the spectra in the less overlapped region, for frequencies lower than 70 cm^{-1}. On the other hand, the spectrum of each mixed crystal shows notorious differences with respect to the corresponding mechanical mixture, indicating also that phase segregation is not appreciable in these systems. In general, the Raman spectra of mixed crystals result was more similar to the spectrum of BClPS than BBrPS, as would be expected for the case of a solid with a crystal structure close to BClPS hosting diluted-BBrPS molecules. There are changes in the spectra with respect to pure BClPS affecting frequency, intensity, and linewidth of the resolvable peaks, especially for concentrations 0.15 and 0.30. The broadening of the observed peaks is expected due to the introduction of a degree of disorder in the crystal structure.

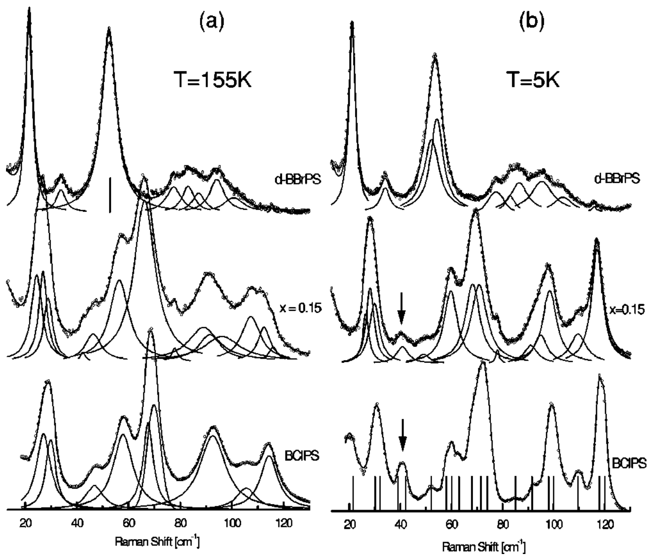

FIG. 5. Raman spectra of BCIPS, the mixed-crystal sample $x = 0.15$, and d-BBrPS taken at (a) 155 and (b) 5 K. Deconvoluted vibrational bands are shown in each case. For the 5-K spectrum of BCIPS only the centers of deconvoluted vibrations are indicated with vertical lines. Arrows point to the more conspicuous bands of the IC phase detected in BCIPS and in the mixed crystal.

Low-temperature measurements were performed with a sample $x = 0.15$ in order to deal with a narrower vibrational spectrum. Figure 5(a) shows the spectrum of the mixed crystal with $x = 0.15$ at 155 K, compared with the pure phases at the same temperature. A multiple-Lorentzian fitting performed on the Raman spectrum showed at least 14 bands in this mixed crystal, instead of the nine bands found in pure phases. This observation corresponds to the so-called two-mode behavior of vibrations in mixed crystals.[24] In this type of crystal, two sets of phonons can be identified, with frequencies close to those of the pure components. This behavior is found in crystals with short-range interactions between building units, for example covalent diatomic crystals such as $Si_{x-1}Ga_x$,[24] and it is also expectable in Van der Waals mixed crystals. There is a set of vibrations in the spectrum of sample $x = 0.15$ with frequencies coinciding with, or very close to (less than 2 cm^{-1}), the values of BClPS vibrations. The remaining lines can be related with BBrPS vibrations, but with larger frequency shifts (up to 8 cm^{-1}). Table I shows a possible correlation among phonon frequencies of pure components and the mixed crystal with $x = 0.15$. For lines above 80 cm^{-1}, the strong overlap precludes a reliable identification of vibrations and their correlations. According to results in binary covalent alloys, the substitution for the lighter mass with a heavier impurity gives rise to an optical gap and localized modes.[24] In BClPS, lattice-dynamics calculations suggest that there is no gap between optical and acoustical phonons.[10] Therefore, additional lines in the mixed crystals should be associated with localized modes of BBrPS in the BClPS hosting lattice.

The Raman spectrum of the mixed crystal with $x = 0.15$ was measured at low temperature, in order to obtain information about its structural stability. Figure 1(d) shows the observed Raman spectra, performing the experiments in order of decreasing temperatures. After the total temperature cycle (slow cooling to 5 K and subsequent heating to room temperature), no differences were found in the Raman spectrum at room temperature with respect to the beginning of the experiment, indicating the stability of the mixture. On lowering temperature, several continuous changes in the Raman spectrum of the mixed crystal can be observed, as in the case of BClPS: the appearance of the band at 40 cm^{-1} and modifications in the relative intensity of bands in the 80–120 cm^{-1} region. In Fig. 5(b), the spectra at 5 K of the pure components and the mixed crystal are compared. Spectra of BClPS and $x = 0.15$ samples are almost identical, apart from a shift to low frequency (3 cm^{-1}) of some peaks in the mixture. The band at 40 cm^{-1} is clearly resolved in the mixed crystal, though its relative intensity is smaller than in BClPS. This band can be detected between 5 and 105 K. The above similarities indicate that the $x = 0.15$ mixed crystal also undergoes an IC phase transition. Though this experiment is not very sensitive to determine the transition point, it seems that transition temperatures in the mixed crystal and BClPS do not differ very much, considering that new bands and intensity variations are detected at the same temperatures in both systems. On the other hand, the lower intensity of the IC band at 40 cm^{-1} could indicate structural distortions of the periodic structure with smaller amplitudes with respect to those present in the IC phase of pure BClPS.

TABLE I. Frequency of deconvoluted vibrations at 155 K for BClPS, BBrPS, and the mixed crystal with $x = 0.15$.

BClPS (cm^{-1})	$x = 0.15$ (cm^{-1})	d-BBrPS (cm^{-1})
	24	21.4
27	27	
30	29	
	42	33.6
46.8	46	
57.8	56	51.5 (doublet)
69.7/67.4	66	
	78	77.2
	86	80/85
92.6	91	
	95	94
105.5	107	102
114.4	112	
	116	115.5
151.5	151	

IV. CONCLUSIONS

Information about the low-temperature structural and dynamical behavior of PS and BBrPS was obtained. The results presented for these two solids agree with the proposal of an intrinsic mechanical instability of BClPS-like molecular packings. For PS, previous lattice-dynamic calculations carried out on the room-temperature structure and on a relaxed zero-Kelvin structure have not revealed any phonon instability.[10] Accordingly, Raman spectroscopy measurements down to 5 K did not show any loss of periodicity or change in the symmetry of the room-temperature cell. For BBrPS, where lattice-dynamic calculations pointed out the possibility of a phonon softening at low temperatures, deuteron spin-lattice relaxation data showed an anomalous enhancement of relaxation rates between 157 and 148 K. The values assumed by T_1^{-1} and its temperature behavior agree with those observed near the transition temperature in BClPS. Also, the experimental data are compatible with a model of the spectral densities resulting from a soft-mode process in addition to central-peak effects. Considering the set of dynamical parameters obtained for the soft mode of the IC PT in BClPS by means of INS, the model reproduces the observed temperature behavior of the relaxation rate measured in BBrPS. It is worth noting that the soft-mode contribution alone cannot account for the observed temperature behavior of T_1^{-1} in BBrPS. The results also suggest the possibility that the coupling between the soft phonon and the relaxing mode becomes appreciable for temperatures lower than those in BClPS. On the other hand, Raman spectroscopy measurements in BBrPS did not show any strong loss of periodicity, as in the IC phase of BClPS, nor changes in the symmetry of the unit cell down to 5 K. Therefore, the PT in BBrPS should involve only small amplitude distortions of the room-temperature structure, compatible with the symmetry of the unit cell.

On the other hand, solubility of BBrPS molecules in the BClPS structure provides a way to perturb the balance of intermolecular interactions affecting the lattice instability. The presented results show that solid solubility exists at least up to the ratio $[d\text{-BBrPS/BClPS}]=0.30$. From the Raman spectrum profile and the powder x-ray diffractograms, the structure of these mixed crystals is closely related to BClPS. Local modes associated with the BBrPS ''impurities'' can be detected in the Raman spectra. The low-temperature behavior of the mixed crystal with $x=0.15$ is very similar with respect to BClPS. This mixed system undergoes an incommensurate phase transition, at a temperature very similar to the PT of BClPS, with a smaller amplitude of the IC distortion. This behavior suggest a continuous trend of the phase diagram as a function of x, from relatively large displacement amplitudes in BClPS to small distortions in BBrPS. The results show that the critical temperature in BClPS-like solids does not vary strongly, being around 148 K. Additional experimental effort will be devoted to trace the evolution of the IC distortions over the full concentration range.

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